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(54) **Process for producing hard stocks.**

(57) A process for producing hard stocks comprises the step of allowing a lipase to act on a mixture of palm type oils, lauric type oils, and behenic acid or esters thereof for interesterification.

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The present invention relates to a process for producing hard stocks which are useful as raw materials for plastic fat products such as margarine and shortening.

Most plastic fat products such as margarine and shortening are produced from hard stocks and liquid oils as raw materials. As an example of such a production method liquid oils such as soybean oil, corn oil, and rapeseed oil, are blended with their hardened oils (hard stocks), and the blend is adjusted so as to have an appropriate consistency (plasticity). The plastic fat products such as margarine and shortening thus produced tend to cause the formation of relatively coarse crystallines because fats and oils used as the raw materials are composed of fatty acids having almost the same carbon chain length, in other words, they have a highly-uniform composition of fatty acids. For this reason, the plasticity of the products can be maintained at an appropriate level only within a narrow temperature range, so that the liquid oils contained therein have a tendency to exude.

As a process for producing other hard stocks useful as a raw material of plastic fat products such as margarine and shortening, there is a well-known process using palm type oils, in which palm type oils and lauric type oils are subjected to random interesterification with a metallic catalyst such as sodium methylate (see, e.g., US-A-3 949 105). According to this process, the fundamental symmetrical structure of palm type oils can be modified into a random structure, and it is, therefore, possible to improve the properties of plastic fat products which will become unfavorable because the palm type oils may be gradually hardened with time when the products are being stored. However, an increase in the amount of undesirable tri-saturated triglycerides causes an inevitable rise in melting point, and various characteristics as a plastic fat material are deteriorated by the formation of coarse crystallines; accordingly, the products may have poor characteristics of melting in the mouth. For this reason, fractionation or hardening is required after the interesterification.

If the interesterification is conducted with a lipase (see EP-A-0 170 431), which has, in particular, a selectivity for the 1- and 3-positions of triglycerides, it is possible to inhibit an increase in the amount of tri-saturated triglycerides. According to this process, however, palm type oils remain having the fundamental symmetrical structure, i.e., having a tendency to crystallize in the β-form, so that a sufficient improvement in the crystallizability as a hard stock material for use in margarine and shortening cannot be attained. This causes the problem that when used as a raw material of plastic food the plasticity of the food will deteriorate during storage.

Under these circumstances, in order to solve the above problems, the present inventors have intensively studied a process for producing hard stocks with excellent characteristics by use of palm type oils which are abundant and inexpensive. As a result, they have found that both the above deficiency of conventional random interesterification and the difficulty of interesterification with a lipase can be solved by conducting interesterification which has a specificity for the 1- and 3-positions of triglycerides in the presence of behenic acid residues as well as lauric type oils. That is, they have found that it is possible to prevent the exudation with temperature increase of liquid oils contained in the products, to inhibit a rise in the melting point caused by an increase in the amount of tri-saturated triglycerides, and to solve the problem that the products may harden with time during long-term storage, thereby arriving at the present invention.

Thus, the present invention provides a process for producing hard stocks with excellent characteristics for use as a raw material of plastic fat products, based on interesterification with a lipase which is allowed to act on a mixture of palm type oils, lauric type oils, and behenic acid or esters thereof.

This benefit as well as other advantages of the present invention will become apparent to those skilled in the art from the following description.

According to the present invention, there is provided a process for producing hard stocks comprising the step of allowing a lipase to act on a mixture of palm type oils, lauric type oils, and behenic acid or esters thereof for interesterification.

The mixture subjected to interesterification in a preferred embodiment has a fatty acid composition of 6-25%lauric acid, 23-48% palmitic acid, and 0.5-5% behenic acid.

The palm type oils used in a preferred embodiment are selected from palm oil, fractioned oils and hardened oils thereof.

The lauric type oils used in a preferred embodiment are selected from palm kernel oil, coconut oil, babassu oil, fractioned oils and hardened oils thereof.

The lipase used in a preferred embodiment is selected from lipases derived from the genus Rhizopus, Aspergillus or Mucor, pancreatic lipase, and rice bran lipase.

The palm type oils used in the present invention are those having a palmitic acid content of 30% or more, examples of which are palm oil per se, fractioned oils and hardened oils thereof. The lauric type oils used in the present invention are those having a lauric acid content of 30% or more, examples of which are palm kernel oil, coconut oil, babassu oil, fractioned oils and hardened oils thereof. The behenic acid is in the form of a free fatty acid, and esters thereof are those formed from behenic acid with a monohydric or polyhydric alcohol, for example, in the form of a fatty acid ester of alcohols such as methanol, ethanol, ethylene glycol, and glycerol.

In addition to the above palm type oils and lauric type oils, any other oil may be used as a starting oil for

interesterification. It is, however, preferred that a mixture of these starting oils for interesterification is adjusted to have a fatty acid composition of 6-25% lauric acid, 23-48% palmitic acid, and 0.5-5% behenic acid. Such a fatty acid composition makes it possible to provide hard stocks useful as a raw material of plastic fat products; the hard stocks have a melting point of from 30°C to 45°C, high malleability and high ductility, as well as excellent properties of preventing the exudation of liquid oils within a temperature range of from room temperature to a temperature slightly higher than room temperature. Moreover, they can preferably prevent, when used as a hard stock material of plastic fat products, the deterioration of plasticity.

In particular, to achieve an efficient production of hard stocks having excellent properties of melting in the mouth, without using the step of fractionation or hardening after the interesterification, for example, the following blend of raw materials with a fatty acid composition as described above can be employed: 13-50% palm oil or stearin fractions obtained by fractionation thereof as a palm type oil, 48-85% palm kernel oil, coconut oil, babassu oil, or olein fractions obtained by fractionation thereof as a lauric type oil, and 2-10% hardened oils having a behenic acid content of 20% or more as a behenic acid component.

The process of the present invention is based on the interesterification of a mixture comprising palm type oils, lauric type oils, and behenic acid or esters thereof with a lipase. Therefore, the carbon chain length in the constituent fatty acids of mixed fatty acid triglycerides formed may vary widely, and even if there remains the structure having oleic acid at the respective 2nd positions of the palm type oils in a relatively high proportion, the resulting hard stocks have excellent advantages of inhibiting the formation of coarse crystallines with time, having good crystallizability as a plastic fat, and exhibiting satisfactory plasticity when used in a product such as margarine.

The lipase used for interesterification preferably has a specificity for the 1- and 3-positions of triglycerides because the formation of undesirable tri-saturated triglycerides is reduced and the carbon chain length in the constitute fatty acids as described above widely varies, so that excellent physical properties can be retained even after a long-term storage. Examples of the lipase with a specificity for the 1- and 3-positions of triglycerides are those derived from the genus Rhizopus, Aspergillus or Mucor, pancreatic lipase, and rice bran lipase. Although these lipases can be used in a free form for the interesterification, it is usually preferred that they are used in an immobilized form by adsorbsion on a support such as diatomaceous earth, alumina, or active carbon.

Also, lipases in the form of a dried enzyme preferably prepared as disclosed in US-A-4 472 503 and US-A-4 873 194 have an activity even in the absence of water, and the use of such a dry enzyme can make it possible to reduce the formation of by-products from side reactions, such as diglycerides, in the reaction system. The interesterification is conducted in a batch or continuous process with or without solvent at a temperature of from 20°C to 70°C.

The following examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof. Unless otherwise indicated, parts and percentages (%) are all by weight.

Example 1 and Comparative Examples 1-3

At a proportion shown in Table 1 below, palm stearin, palm oil, palm kernel olein, and highly hardened high-erucic rapeseed oil were mixed together, and the mixture was subjected to interesterification with a lipase having a specificity for the 1- and 3-positions of triglycerides, resulting in a hard stock (Example 1).

For comparison, were prepared an interesterified fat obtained without blending highly hardened high-erucic rapeseed oil (Comparative Example 1), an oil blend having the same composition as that of Example 1 and obtained without any interesterification (Comparative Example 2), and hardened soybean oil (Comparative Example 3). The analytical data of the fatty acid composition of these hard stocks and the physical properties are also shown in Table 1.

Then, 50 parts of each of the above hard stocks were blended with 50 parts of purified soybean oil, and 80 parts of this blend were further blended with an aqueous phase comprising water, powdered skim milk, and common salt to produce margarine by a conventional process. The margarine was stored at 5°C or 25°C, and the physical properties were evaluated. The results are shown in Table 2. A change in hardness with time was determined by measurements with a rheometer (manufactured by Fudo Kogyo Co, Ltd.) using a 10 mmϕ plunger at a table-rise rate of 5 cm/min.

Table 1

	Example 1	Comparative Example 1	Comparative Example 2	Comparative Example 3
Preparation method	Interesterification	Interesterification	Blending	Hardening
Raw materials (parts)				
Hardened soybean oil	-	-	-	100
Palm stearin	34	35	34	-
Palm oil	24	25	24	-
Palm kernel olein	39	40	39	-
Highly hardened high-erucic rapeseed oil	3	-	3	-
Fatty acid content (%)				
Lauric acid	15.6	16.0	15.6	0
Palmitic acid	32.1	33.2	32.1	10.2
Behenic acid	1.5	0	1.5	0
Physical properties				
Iodine value	35.2	36.3	35.3	75.8
Melting point (°C) (softening point)	34.1	34.5	46.0	34.0
Solid fat index (%)				
at 5°C	35.9	36.7	37.1	34.2
at 10°C	30.4	29.8	29.7	31.9
at 15°C	25.4	23.8	25.3	28.2
at 20°C	23.1	20.3	24.2	23.9
at 25°C	16.6	14.2	23.2	16.8
at 30°C	9.5	8.1	21.2	7.3
at 35°C	3.7	3.9	19.4	1.6
at 40°C	0.2	0.5	15.8	0.0
at 45°C	0.0	0.0	10.0	0.0
at 50°C	0.0	0.0	0.5	0.0

Table 2

	Example 1	Comparative Example 1	Comparative Example 2	Comparative Example 3
Separation of liquid oils (25°C)*				
after 3 days	-	-	-	+
after 7 days	-	-+	-	+
Change in hardness with time (5°C)				
after 10 days	400	500	630	360
after 30 days	420	950	1200	400
after 90 days	480	1500	1860	430
evaluation	small	large	large	small
Malleability and ductility (after storage at 5°C)	good	good	poor	good

* Criteria of evaluation: -, no separation; -+, slight separation; +-, moderate separation; and +, significant separation.

As seen from the results in Table 2, the margarine using hardened soybean oil (Comparative Example 3) caused the separation of liquid oils at 25°C; the margarine using an interesterified oil of the palm/lauric type (Comparative Example 1) also caused the separation of liquid oils in some degree and exhibited a significantly large change in hardness with time, thereby causing deterioration of plasticity. Although the use of behenic acid residues in part of the raw materials prevented the separation of liquid oils, the oil blend prepared without any interesterification (Comparative Example 2) exhibited inferior characteristics of melting in the mouth, poor malleability and poor ductility, as well as a significantly large change in hardness with time, thereby causing deterioration of plasticity.

In contrast, the hard stock prepared using behenic acid residues by interesterification (Example 1) provided a margarine which did not cause separation of liquid oils and exhibited only a quite small change in hardness. This fact indicates that all the above disadvantages of Comparative Examples 1-3 were solved by a combination of the use of behenic acid residues with interesterification.

Examples 2-5 and Comparative Examples 4-6

Various kinds of margarine were produced in the same manner as described in Example 1, except that the raw materials shown in Table 3 were used and interesterification was conducted in all cases. In Example 5 where ethyl behenate was used in place of highly hardened high-erucic rapeseed oil, there was a need to remove ethyl ester fractions by distillation after the interesterification.

Table 3

	Example 2	Example 3	Example 4	Example 5
Preparation method	Interesterification	Interesterification	Interesterification	Interesterification
Raw materials (parts)				
Palm stearin	5	5	7	4.5
Palm oil	78	48	55	79
Palm kernel oil		45		
Palm kernel olein	15		30	15
Highly hardened high-erucic rapeseed oil	2	2	8	
Ethyl behenate				1.5
Fatty acid content (%)				
Lauric acid	6.2	21.6	12.3	6.2
Palmitic acid	38.5	27.6	30.5	41.7
Behenic acid	1.0	1.0	4.0	1.5
Physical properties				
Iodine value	47.0	34.7	36.3	46.5
Melting point (°C) (softening point)	34.1	34.8	42.3	34.5

Table 3 (cont'd)

	Comparative Example 4	Comparative Example 5	Comparative Example 6
Preparation method	Interester-ification	Interester-ification	Interester-ification
Raw materials (parts)			
Palm stearin	10		
Palm oil	78	43	55
Palm kernel oil		55	
Palm kernel olein	10		30
Highly hardened high-erucic rapeseed oil	2	2	15
Ethyl behenate			
Fatty acid content (%)			
Lauric acid	4.1	26.4	12.3
Palmitic acid	40.8	18.9	24.2
Behenic acid	1.0	1.0	7.5
Physical properties			
Iodine value	48.4	31.7	31.0
Melting point (°C) (softening point)	34.0	34.4	42.1

Table 4

	Example 2	Example 3	Example 4	Example 5
Separation of liquid oils (25°C)*				
after 3 days	-	-	-	-
after 7 days	-	-	-	-
Change in hardness with time (5°C)	small	small	small	small
Malleability and ductility (after storage at 5°C)	good	good	good	good
Characteristics of melting in the mouth	good	good	good	good

* Criteria of evaluation: -, no separation; -+, slight separation; +-, moderate separation; and +, significant separation.

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Table 4 (cont'd)

	Comparative Example 4	Comparative Example 5	Comparative Example 6
Separation of liquid oils (25°C)*			
after 3 days	-	-	-
after 7 days	-+	-+	-
Change in hardness with time (5°C)	large	large	small
Malleability and ductility (after storage at 5°C)	poor	poor	good
Characteristics of melting in the mouth	poor	good	poor

* Criteria of evaluation: -, no separation; -+, slight separation; +-, moderate separation; and +, significant separation.

As seen from the results in table 4, when the lauric acid content was smaller than 6% (Comparative Example 4), malleability and ductility became poor; characteristics of melting in the mouth deteriorated; physical properties significantly changed with time; and slight separation of liquid oils was caused. On the other hand, when the lauric acid content was greater than 25% (Comparative Example 5), satisfactory characteristics of melting in the mouth were attained, whereas other physical properties deteriorated. These facts indicate that lauric acid contents outside the range of from 6% to 25% produce only a small effect of long-chain fatty acids.

The margarine produced from the hard stock with a behenic acid content greater than 5% (Comparative Example 6) also had inferior characteristics of melting in the mouth.

As described hereinabove, hard stocks obtained by the process of the present invention are particularly useful as a raw material of plastic fat products such as margarine and shortening because they have the excellent advantages of inhibiting the separation of liquid oils, having satisfactory characteristics of melting in the mouth, and preventing deterioration of plasticity with time.

Claims

1. A process for producing hard stocks comprising the step of allowing a lipase to act on a mixture of palm type oils, lauric type oils, and behenic acid or esters thereof for interesterification.

2. A process as claimed in claim 1, wherein said mixture has a fatty acid composition of 6-25% lauric acid, 23-48% palmitic acid, and 0.5-5% behenic acid.

3. A process as claimed in claim 1 or claim 2, wherein said palm type oils are selected from palm oil, fractioned oils and hardened oils thereof.

4. A process as claimed in claim 1 or claim 2, wherein said lauric type oils are selected from palm kernel oil, coconut oil, babassu oil, fractioned oils and hardened oils thereof.

5. A process as claimed in any one of the preceding claims wherein said lipase is selected from lipases derived from the genus Rhizopus, Aspergillus or Mucor, pancreatic lipase, and rice bran lipase.

6. Use of hard stocks produced by the process as claimed in any one of claims 1 to 5 in plastic fat products such as margarine and shortening.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 5918

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,Y	EP-A-0 170 431 (UNILEVER N.V.) * page 1 - page 7; claims 1-4,11 * * page 8, line 26 - line 34 * ---	1-6	A 23 D 7/00 C 11 C 3/10
Y	PATENT ABSTRACTS OF JAPAN vol. 6, no. 154 (C-119)(1032) 14 August 1982 & JP-A-57 074 041 (ASAHI DENKA KOGYO K.K.) 10 May 1982 * abstract * ---	1-6	
A	PATENT ABSTRACTS OF JAPAN vol. 7, no. 191 (C-182)(1336) 20 August 1983 & JP-A-58 094 345 (KAO SEKKEN K.K.) 4 June 1983 * abstract * ---	1-3,6	
A	FR-A-2 570 388 (DANIEL GERSCHEL) * the whole document * ---	1,3-4,6	
A	EP-A-0 427 309 (UNILEVER N.V.) * claims 1-2,4 * ---	1	
D,A	US-A-3 949 105 (T.WIESKE) * the whole document * ---	1,3-4,6	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	EP-A-0 151 450 (UNILEVER N.V.) * page 3, line 5 - line 25 * * page 4, line 4 - line 20 * -----	1,3-4,6	A 23 D C 11 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	15-09-1992	ALVAREZ Y ALVAREZ C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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